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(54) **Low coefficient of friction silicone release formulations**

Silikontrennschichtformulierungen mit niedrigem Reibungskoeffizienten

Formulations de polyorganosiloxanes antiadhésives à coefficient de friction bas

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EP 0 903 385 B1

Description

[0001] The invention relates to silicone release coatings.

[0002] Release coatings are useful for many applications whenever it is necessary to provide a surface or material which is relatively non adherent to other materials which would normally adhere thereto. Silicone paper release compositions are widely used as coatings which release pressure-sensitive adhesives for labels, decorative laminates or transfer tapes. Silicone release coatings on paper, polyethylene, Mylar and other such substrates are also useful as non-stick surfaces for food handling and industrial packaging applications.

[0003] For example, when labels are coated with an adhesive, it is desirable that the paper backing be easily peeled away from the label when it is ready for use, yet the adhesive quality of the label should not be reduced by peeling it away from the substrate upon which it was stored. The same principle applies to certain types of adhesive tapes which come in rolls. It is necessary that the tape unroll easily and still maintains its adhesive characteristics. This can be accomplished by coating the non-adhesive side of the tape with a silicone release composition which will come into contact with the adhesive as the roll of tape is manufactured.

[0004] US-A-5482780 discloses polypropylene film with cold seal release and cold seal receptive surfaces. The cold seal release skin layer comprises a slip agent and a blend of an ethylene-propylene random copolymer and an ethylene-butylene copolymer. The slip agent includes talc, micron sized silicas, glass beads, diatomaceous earth and clay.

[0005] WO/96/18497 discloses a multi layer oriented heat sealable film structure which includes at least one layer of an olefin homo-, co- or ter-polymer having a surface-treated external surface which is printable, sealable and machinable, the layer containing, as combined slip agent and antiblock, a particulate crosslinked hydrocarbyl-substituted polysiloxane, preferably a crosslinked polymonoalkylsiloxane, and/or liquid polydimethyl siloxane.

[0006] EP-A-0471589 discloses a curable silicon rubber composition comprising a vinyl functional polyorganosiloxane, a silicone powder containing 3-80 mol% $R^1{}_3SiOSiO_{3/2}$ units and 97-20 mol% $R^2SiO_{3/2}$ units where R^1 and R^2 are independently monovalent substituted or unsubstituted hydrocarbon group having 1 to 10 carbon atoms and having a mean particle size of 0.05-20 μm and a curing agent.

[0007] Substrates coated with standard silicone release formulations have a relatively high coefficient of friction. When a coated substrate is transported on static steel rolls, obstruction of the rolls and deformation of the coated substrate can occur, due to the high coefficient of friction. The formulation of this invention reduces the coefficient of friction to a very low value, while substantially maintaining the release properties of the silicone release coating. This allows transport of a fully effective silicone release coated substrate on, for example, static steel rolls without any problems.

[0008] Most silicone release coatings have a glossy surface. An additional feature of the silicone release coatings obtained from the invention is a mattee finish surface, which is advantageous for use in applications such as decorative films, as the matte finish allows the adhesive to be repositioned.

SUMMARY OF THE INVENTION

[0009] In one aspect, the invention relates to a low coefficient of friction release coating composition comprising: (a) 1000 parts by weight of an epoxy functional polyorganosiloxane; (b) 1 - 100 parts by weight of a highly crosslinked fine particle silicone resin; and (c) 5-50 parts by weight of a photoinitiator;

[0010] In another aspect, the invention relates to a method of reducing coefficient of friction of a silicone release coating, comprising adding spherical silicone resin particles to the silicone release coating, whereby the coefficient of friction is reduced by at least two-fold while the release value is reduced by less than two-fold.

[0011] In another aspect, the invention relates to a substrate coated with a low coefficient of friction release coating formulation.

DETAILED DESCRIPTION OF THE INVENTION

[0012] In its most basic aspect, the invention relates to a method for reducing the coefficient of friction of a silicone release coating without changing the original release properties of the silicone release coating and to a corresponding composition for a release coating with a low coefficient of friction. The improved release coating comprises: (a) an epoxy functional polyorganosiloxane, (b) a fine particle silicone resin, and (c) a photoinitiator.

[0013] The epoxy functional polyorganosiloxane can be any of the w ll-known members of this class. Epoxy functional polyorganosiloxanes suitable for use as silicone release coatings are described in US Patent Nos. 4,279,717, 4,421,904, 4,977,158, 5,085,924, 5,258,480, 5,360,833 and 5,397,813.

[0014] The fine particle silicone resin is composed of a highly crosslinked silicone resin obtained by controlled hydrolysis crosslinking of methyltrimethoxysilane which results in a resin with a network structure in which siloxane bonds extend three-dimensionally. The particles are spherical and characterized by a narrow particle size distribution. "Spher-

ical" as used herein means that the diameter of the particle measured at any point varies by less than 10% from the diameter measured at any other point. The resin is commercially available from Toshiba Silicone Co., Ltd. (Japan) as Tospearl and is described in Japanese Patent No. 4117456. The particle size ranges from 0.5-12 μm, and preferably 2-4.5 μm.

[0015] Suitable photoinitiators for curing of the compositions of the present invention are described in US patent 4,279,717, referenced above. These initiators are iodonium salts with structural modifications which render them compatible with epoxy-functional silicones.

[0016] An example of such a low coefficient of friction release coating formulation is:

(a) 1000 parts by weight epoxy functional polyorganosiloxane;
(b) 1-100 parts by weight fine particle silicone resin; and
(c) 5-50 parts by weight photoinitiator.

[0017] In many preferred embodiments the level of fine particle silicone resin is 1 to 50 part by weight acid to 1000 parts by weight of epoxy functional polyorganosiloxane, and in a particularly preferred embodiment, the fine particle silicone resin is present at about 2 parts by weight per 1000 parts by weight, or 0.2%, of epoxy functional polyorganosiloxane.

Coefficient of Friction

[0018] To demonstrate the efficacy of the low coefficient of friction release coating system of the invention, standard release coating formulations with and without 0.2% of a fine particle silicone resin were prepared, coated on a suitable substrate, cured by exposure to focused UV light, and the coefficient of friction determined.

[0019] The starting formulations of the release coating were:

100 parts by weight of epoxy functional polyorganosiloxane
2 parts photoinitiator
0.2 parts fine particle silicone resin

[0020] The photoinitiator employed in the test compositions was UV9380C, a cationic photoinitiator activated by UV radiation.

[0021] The components were thoroughly mixed, applied to a polyester (PET) substrate at a coatweight of about 1 gram per square meter using a Dixon coater, and cured under 300W/in Fusion H ultraviolet lamps at a line speed of 15 meters per minute. Table 1 shows the results of the testing of the standard formulations and the standard formulations with 0.2% fine particle silicone resin.

[0022] The following definitions and abbreviations are employed in the Tables:

UV9315, UV9400, and UV9500 are the commercial designations of the polysiloxanes described above. They may be generically described as dimethylepoxysilyloxy-stopped linear polydimethylmethylepoxysiloxane, where the epoxy group is a 3,4-epoxy-2-ethyl-cyclohexyl group. The composition UV9500 is taught in US Patent 5,397,813. The resins are available from General Electric Silicones. Another epoxy-functional siloxane useful in these compositions is sold by GE Silicones as UV9300. It is described in US Patent 4,421,904 above.
T120 is Tospearl 120, a fine particle silicone resin commercially available from Toshiba Silicone Co., Ltd.

Table 1

PRODUCT FORMULATION	COEFFICIENT OF FRICTION (no units)
UV9500 + 0.2% T120	0.356
UV9400 + 0.2% T120	0.277
UV9315 + 0.2% T120	0.313
UV9500	1.605
UV9400	Out of Scale
UV9315	1.216

[0023] From Table 1, it can be seen that the coefficient of friction of the release coating was dramatically lower for the compositions with the fine particle silicone resin. The coefficient of friction was reduced over the controls by a factor of at least three. It should be clear to those skilled in the art that high release epoxy-silicone compositions such as those taught in US Patent 5,360,833 may also be treated with low concentrations of fine particle silicone resin for the purpose of reducing the coefficient of friction of cured coatings of such materials.

Release Values

[0024] The effect of incorporating fine particle silicone resin on release properties of the coating was determined. Various levels of fine particle silicone resin, from 1 to 50 parts per 1000 were added to the formulation, as shown in Table 2. The standard formulation described previously was used. The coating was applied to a biaxially oriented polypropylene (BOPP) substrate and cured. Laminates of a pressure sensitive adhesive tape and BOPP substrate coated with the experimental formulations were prepared and the release values were determined by using an IMASS Slip/Peel tester. The results are shown in Table 2.

[0025] The following definitions and abbreviations are employed in the Table:

UV9315 is the commercial designation of a polysiloxane described above. It is available from General Electric Silicones.
TESE 7475, TESE 4154, and TESA 7476 are commercially available acrylic pressure sensitive adhesive tapes available from Beiersdorf AG, Hamburg, Germany.
T120 is Tospearl 120, a fine particle silicone resin commercially available from Toshiba Silicone Co., Ltd.

Table 2

PRODUCT FORMULATION	RELEASE VALUE, cN/mm					
	TESE7475		TESE4154		TESA7476	
	1 Day	7 Days	1 Day	7 Days	1 Day	7 Days
UV9315 + 0.1% T120	6	8	14	19	28	45
UV9315 + 0.5% T120	10	13	27	28	35	51
UV9315 + 1.0% T120	6	9	18	20	29	45
UV9315 + 2.0% T120	8	10	24	30	35	55
UV9315 + 5.0% T120	9	11	25	28	35	60
UV9315	8	10	15	23	33	58
UV9315 + 0.1% T120	18	14	8	24	32	52
UV9315 + 0.5% T120	29	17	12	35	38	60
UV9315 + 1.0% T120	20	10	7	25	34	52
UV9315 + 2.0% T120	34	13	8	44	41	72
UV9315 + 5.0% T120	36	13	10	40	42	62
UV9315	18	11	9	23	38	59

[0026] From Table 2, it is apparent that the addition of up to 5% fine particle silicone resin does not materially affect the release value of the coating for any of the pressure sensitive adhesives tested, under normal aging conditions.

[0027] Although this invention is susceptible to an embodiment in many different forms, preferred embodiments of the invention are described above. It should be understood, however, that the present disclosure is to be considered as an exemplification of the principles of this invention and is not intended to limit the invention to the embodiments described. The particular epoxy functional polyorganosiloxanes shown above in the examples were chosen simply on the basis of their ready commercial availability and cost. Similarly, other compatible cationic photoinitiators would function analogously to that illustrated above; it was also chosen on the basis of its ready availability and cost.

[0028] For the preparation of a low coefficient of friction silicone release coating composition, one mixes an epoxy functional polyorganosiloxane, a photoinitiator, and a fine particle silicone resin. A coated article is prepared by mixing the components, spreading the coating composition on the substrate and curing the coated article by exposure to

ultraviolet light, all of which are carried out by means well known in the art.

Claims

1. A release coating composition comprising:

   (a) 1000 parts by weight epoxy functional polyorganosiloxane;
   (b) 1-100 parts by weight spherical fine particle silicone resin comprising a highly crosslinked silicone resin obtained by controlled hydrolysis crosslinking of methyltrimethoxy silane which results in a resin with a network structure in which siloxane bonds extend three-dimensionally, having a particle size of 0.5-12 μm; and
   (c) 5-50 parts by weight photoinitiator.

2. A release coating composition according to claim 1 comprising:

   (a) 1000 parts by weight epoxy functional polyorganosiloxane;
   (b) 1-50 parts by weight spherical fine particle silicone particles;
   (c) 10-30 parts by weight photoInitiator.

3. A release coating composition according to claim 1 comprising:

   (a) 1000 parts by weight epoxy functional polyorganosiloxane;
   (b) 2 parts by weight spherical fine particle silicone resin; and
   (c) 20 parts by weight photoinitiator.

4. The composition of any preceding claim wherein said polyorganosiloxane is a dialkyl epoxysiloxy chain-stopped polydialkylalkylepoxy siloxane.

5. The composition of claim 4 wherein said polyorganosiloxane is a dimethylepoxysiloxy chain-stopped polydimethyl-methylepoxy siloxane.

6. The composition of any preceding claim wherein the particle size of said silicone particle is 2 - 4.5 μm.

7. The composition of any preceding claim wherein the particle size of said silicone particle is 2 μm.

8. A method of reducing coefficient of friction of a silicone release coating, comprising adding to said silicone release coating from 1 to 100 parts by weight of spherical silicone resin particles per 1000 parts of said silicone release coating, said spherical silicone resin particles comprising a highly crosslinked silicone resin obtained by controlled hydrolysis crosslinking of methyltrimethoxy silane which results in a resin with a network structure in which siloxane bonds extend three-dimensionally, having a particle size of 0.5-12 μm.

9. A substrate with a coating obtained by using the formulation of any preceding claim.

Pat ntansprüche

1. Trennmittelüberzugs-Zusammensetzung, umfassend:

   (a) 1.000 Gewichtsteile epoxyfunktionelles Polyorganosiloxan,
   (b) 1-100 Gewichtsteile kugelförmiges feinteiliges Siliconharz, umfassend ein stark vernetztes Siliconharz, erhalten durch kontrolliertes Hydrolyse-Vernetzen von Methyltrimethoxysilan, was zu einem Harz mit einer Netzwerkstruktur führt, bei dem sich Siloxan-Bindungen dreidimensional erstrecken, und mit einer Teilchengröße von 0,5-12 μm, und
   (c) 5-50 Gewichtsteile Fotoinitiator.

2. Trennmittelüberzug-Zusammensetzung nach Anspruch 1, umfassend:

   (a) 1.000 Gewichtsteile epoxyfunktionelles Polyorganosiloxan,

(b) 1-50 Gewichtsteile kugelförmige feine Silicon-Teilchen,
(c) 10-30 Gewichtsteile Fotoinitiator.

3. Trennmittelüberzug-Zusammensetzung nach Anspruch 1, umfassend:

(a) 1.000 Gewichtsteile epoxyfunktionelles Polyorganosiloxan,
(b) 2 Gewichtsteile kugelförmige feine Silicon-Teilchen und
(c) 20 Gewichtsteile Fotoinitiator.

4. Zusammensetzung nach einem vorhergehenden Anspruch, bei dem das Polyorganosiloxan ein Polydialkylalkyl-epoxysiloxan mit Dialkylepoxysiloxy-Endgruppen ist.

5. Zusammensetzung nach Anspruch 4, bei dem das Polyorganosiloxan ein Polydimethylmethylepoxysiloxan mit Dimethylepoxysiloxy-Endgruppen ist.

6. Zusammensetzung nach einem vorhergehenden Anspruch, worin die Größe der Silicon-Teilchen 2-4,5 µm beträgt.

7. Zusammensetzung nach einem vorhergehenden Anspruch, worin die Größe der Silicon-Teilchen 2 µm beträgt.

8. Verfahren zum Verringern des Reibungskoeffizienten eines Silicon-Trennüberzuges, umfassend das Hinzugeben von 1-100 Gewichtsteilen kugelförmiger Siliconharz-Teilchen pro 1.000 Teile des Silicon-Trennüberzuges zu dem Silicon-Trennüberzug, wobei die kugelförmigen Siliconharz-Teilchen ein stark vernetztes Siliconharz umfassen, erhalten durch kontrolliertes Hydrolyse-Vernetzen von Methyltrimethoxysilan, was zu einem Harz mit einer Netzwerkstruktur führt, bei dem sich Siloxan-Bindungen dreidimensional erstrecken, und mit einer Teilchengröße von 0,5-12 µm.

9. Substrat mit einem Überzug, erhalten durch Benutzen der Formulierung nach einem vorhergehenden Anspruch.

Revendications

1. Composition de revêtement de décollement comprenant :

(a) 1000 parties en poids d'un polyorganosiloxane à fonctions époxy ;
(b) 1 à 100 parties en poids de résine silicone sous forme de fines particules sphériques comprenant une résine silicone très réticulée obtenue par réticulation par hydrolyse contrôlée d'un méthyltriméthoxysilane, ce qui conduit à une résine présentant une structure de réseau dans laquelle des liaisons siloxanes s'étendent dans les trois dimensions, et présentant une taille de particules de 0,5 à 12 µm ; et
(c) 5 à 50 parties en poids d'un photoamorceur.

2. Composition de revêtement de décollement selon la revendication 1, comprenant :

(a) 1000 parties en poids d'un polyorganosiloxane à fonctions époxy ;
(b) 1 à 50 parties en poids de silicone sous forme de fines particules sphériques ; et
(c) 10 à 30 parties en poids d'un photoamorceur.

3. Composition de revêtement de décollement selon la revendication 1, comprenant :

(a) 1000 parties en poids d'un polyorganosiloxane à fonctions époxy ;
(b) 2 parties en poids de résine silicone sous forme de fines particules sphériques ; et
(c) 20 parties en poids d'un photoamorceur.

4. Composition selon l'une quelconque des revendications précédentes, dans laquelle ledit polyorganosiloxane est un polydialkyl-alkylépoxysiloxane à groupes terminaux dialkylépoxysiloxy.

5. Composition selon la revendication 4, dans laquelle ledit polyorganosiloxane est un polydiméthyl-méthylépoxysiloxane à groupes terminaux diméthylépoxysiloxy.

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle la taille des particules desdites particules de silicone vaut 2 à 4,5 µm.

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle la taille des particules desdites particules de silicone vaut 2 µm.

8. Procédé pour réduire le coefficient de friction d'un revêtement de décollement de silicone, comprenant l'addition audit revêtement de décollement de silicone, de 1 à 100 parties en poids de particules sphériques de résine silicone pour 1000 parties dudit revêtement de décollement de silicone, lesdites particules sphériques de résine silicone comprenant une résine silicone très réticulée obtenue par réticulation par hydrolyse contrôlée de méthyltriméthoxysilane, ce qui conduit à une résine présentant une structure de réseau dans laquelle des liaisons siloxanes s'étendent dans les trois dimensions, et présentant une taille de particules de 0,5 à 12 µm.

9. Substrat présentant un revêtement obtenu en utilisant la formulation selon l'une quelconque des revendications précédentes.